PCT

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H05K 1/03

A1

(11) International Publication Number: WO 97/14280

(43) International Publication Date: 17 April 1997 (17.04.97)

(21) International Application Number: PCT/US96/16400

(22) International Filing Date: 10 October 1996 (10.10.96)

(30) Priority Data:
08/544,418 10 October 1995 (10.10.95) US

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(81) Designated States: AL, AU, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LK, LR, LS, LT, LV, MG, MK, MN, MW, MX, NZ, PL, RO, RU, SD, SG, SI, SK, TR, TT, UA, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: LAMINATES HAVING IMPROVED DIELECTRIC PROPERTIES

(57) Abstract

Printed circuit boards comprise laminates, e.g. CEM-3 laminates, having insulating substrates which include polymeric particles, particularly core-shell particles having an average diameter of about 0.05 to 30 μm, which reduce the dielectric constant and dissipation factor of such laminates. Comparative Tracking Index (CTI) is significantly improved.

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LAMINATES HAVING IMPROVED DIELECTRIC PROPERTIES

BACKGROUND OF THE INVENTION

The invention relates generally to the field of laminates such as are widely used to make printed circuit boards. More specifically, the invention relates to improved laminates which have lower dielectric properties relative to those made solely of epoxy resins.

The generally recognized types of laminates are discussed in Printed Circuits Handbook, Coombs Ed., Third Edition, McGraw-Hill Book Co., 1988. The lowest cost materials typically use phenolic resin impregnated paper (FR-2) and are used where the cost is more important than the electrical and physical performance. FR-3 is a paper composite which has been impregnated with epoxy resins rather than phenolic resins. CEM-1 is a composite which is more expensive than the FR-2 and FR-3 materials, but which provides improved electrical and physical properties. For CEM-1 an epoxy resin is used to coat paper as in FR-3, but the core is covered with glass fiber reinforced epoxy resin outer layers. CEM-3 uses an epoxy resin impregnated non-woven glass fiber core with epoxy resin impregnated woven glass cloth outer layers. It is a higher cost product and is used in somewhat more demanding applications than is CEM-1. In one aspect the invention comprises an improved CEM-3 laminate for use in high voltage applications, such as in television tuners.

For certain applications it is important to have improved electrical properties, particularly with respect to the dielectric constant and the dissipation factor. The dielectric constant of a material relates to the resistance of that material to an applied voltage. It is defined as the capacitance of the capacitor having a material as a dielectric to the capacitance of a capacitor in which air is the dielectric. Typical values for CEM-3 are given by Coombs to be about 4.6. In other words, the capacitance of the composite is a factor of 4.6 times that of air. The dissipation factor relates to the electrical power which can be lost through a material. It is defined as the ratio of the total power loss in watts in the material to the product of the voltage and current in

a capacitor in which the material is a dielectric. A typical value for CEM-3 at 1 MHz is 0.020 according to Coombs (at Condition A, 10 MHz). The inventors have sought a method of improving the dielectric constant and the dissipation factor for certain applications. Their solution to the problem will be described in detail below.

SUMMARY OF THE INVENTION

In one aspect, the invention is a method of adjusting the dielectric constant and dissipation factor in printed circuit boards, which is accomplished by adding polymeric particles to the thermoset polymers used in the insulating substrates. The polymeric particles preferably are core-shell particles in which a rubbery polymer core is surrounded by a harder polymer shell. The particles typically will represent up to 25 wt.% of the substrate, based on the resin content. Preferably, the particles will be about 5-20 wt.%. A particularly preferred core-shell particle has a average diameter of about 0.05 to 5 μm and has a core comprising a butadiene polymer and a shell comprising a methacrylate polymer.

In another aspect, the invention is a laminate used in printed circuit boards comprising an insulating substrate containing up to 25 wt.% of polymeric particles having an average diameter of about 0.05 to 5 μm. The particles preferably are core-shell particles, especially those having a core comprising a butadiene polymer and a shell comprising a methacrylate polymer.

In still another aspect, the invention is a method of improving the Comparative Tracking Index of insulating substrates used in printed circuit boards comprising incorporating in such insulating substrates up to 25 wt.% of polymeric particles having an average diameter of about 0.05 to 30 μm.

Optionally, inorganic filler particles also may be added to the insulating substrates. Particularly useful are talc and aluminum silicate.

In one embodiment a CEM-3 laminate includes such core-shell particles and is made with an inner layer of non-woven glass fiber reinforced epoxy resin and covering layers of woven glass fiber reinforced epoxy resin.

An alternative embodiment places the woven glass fiber resin in the center, with covering layers of non-woven glass fiber.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The addition of solid particles to epoxy resin compositions has been done to lower the cost of laminates and to gain other advantages. Inorganic particles such as clays, talc, etc. typically are less expensive than epoxy resin and may be used as fillers. There are a number of requirements which should be met. First, the solid particles must be compatible with the components of epoxy varnishes formulated for use in glass reinforced laminates. They should be resistant to aggressive solvents such as DMF and acetone. They should be of a size which permits good dispersion through the mixture. They should not be too large relative to the distance between the circuit lines since they will affect the electrical properties. They should not agglomerate. They should not have significant effect on high temperature tests which laminates must meet, such as solder float. Their density should be similar to that of epoxy resin so that they neither tend to settle or float on the surface. These properties have been found to be satisfied by the polymeric particles described below.

Core-shell Particles

Although the benefits of the present invention may be achieved with the use of particles which have a uniform composition throughout, the preferred particles are those which are commonly called "core-shell" particles. Many types are available. They are usually produced by sequential polymerization as described in many patents and articles of the Rohm and Haas Company. U.S. Pat. No. 3,426,101 describes the process in detail. A recent patent disclosing the use of such particles in amorphous aromatic polyesters to improve impact strength is U. S. Pat. No. 5,409,967. The use of such particles to provide toughening of epoxy resins is also known, as is discussed in the article by B.J. Cardwell and A.F. Yee in Polymer, 1993, Volume 34, Number 8, p. 1695-1701. In U.S. Pat. No. 5,216,077 a rubber-modified phenolic resin is made by heating the resin to soften and to disperse rubber particles in the resin.

The phenolic resin is later combined with an epoxy resin and an inorganic filler for use as an encapsulant, where it is said to have good impact resistance and thermal shock resistance.

Core-shell particles are made by suspension polymerization of a rubbery polymer in which very small seed particles (the core) are produced. Then, the shell is formed over the rubbery core by introducing a monomer which polymerizes to form a hard coating on the surface of the core. This is done under conditions which form little or no separate particles of the shell polymer, but which cause the second monomer to be formed over the core instead.

The particles generally will have an average diameter of about 0.05 to 30 μm, preferably about 0.05 to 5 μm. Although the identity of the polymers is not considered to be critical, a preferred particle has a core of butadiene crosslinked with a second monomer and covered with a shell comprising a methacrylate polymer. The butadiene polymer has good chemical resistance and high temperature; however, it is rubbery and the harder shell polymer is needed to minimize agglomeration and improve mixing with the epoxy resin. However, the shall polymer is more likely to be attacked by the solvents, although this may be advantageous in the present application.

Inorganic particles such as talc, wollastonite (Ca silicate), aluminum hydroxide, and the like may be added if desired. Inorganic fillers are disclosed in U.S. Pat. No. 5,264,065 to be useful in controlling the coefficient of thermal expansion in the Z-axis of laminates, generally using 30 to 100 parts of filler per hundred of resin. Such fillers have been used in laminates for other and related purposes according to the Japanese patent applications discussed in the '065 U.S. patent.

Use of Core-Shell Particles in CEM-3 Laminates

Conventional CEM-3 laminates are made by impregnating a non-woven glass fiber mat with an epoxy resin formulation and then B-staging the impregnated mat. B-staging means that the epoxy resin is partially cured so that it is not tacky and can be handled and stored for some time before being

used to make a finished laminate. Such materials are often called "prepregs". After the mat has been B-staged, covering layers of prepregs made by impregnating woven glass cloth with an epoxy resin formulation are placed on either side of the B-staged mat and the composite is cured to produce a CEM-3 substrate. When assembled with copper foils and other layers of prepreg or fully cured composites they can be cured under heat and pressure to complete the curing process (C-staged). The layers may be reversed, that is, a woven glass cloth may be used in the center with covering layers of non-woven glass fiber mats. Such structures have been found to resist warping and twisting better than conventional CEM-3 constructions.

For certain uses the dielectric constant and dissipation factor of epoxy resin materials are not as low as might be desired. The inventors have sought and have found a method for improving such electrical properties, while at the same time not degrading the usual properties of CEM-3 composites. The objective has been to increase the ability of the epoxy resin to prevent the passage of electricity as defined by the dielectric constant and the dissipation factor, which have been discussed above. Clearly, this will be a desirable characteristic when higher electrical voltages are in use or when the circuit pattern is very dense so that there is little space between the current carrying copper lines. Adding particles which have superior electrical properties has been found to provide the needed improvement to the epoxy laminates, when the amount added is up to about 25 wt.% of the laminate based on the resin content. Greater amounts could further improve the electrical properties but at the expense of the physical properties. Preferably, the amount used should be between about 3 and 20 wt.%, based on the resin content. The particle size is an important factor in obtaining the desired results. The average diameter should be between about 0.05 and 30 μm, preferably about 0.05 and 5 μm. Larger particles will be difficult to distribute uniformly throughout the epoxy resin and would be expected to weaken the structure if too large. The minimum size of the particles is not known, but is presumed to be determined by the method used to make the particles.

Example 1

An epoxy varnish containing 20 parts by weight of core-shell particles per hundred weight of epoxy resin (phr) was prepared by dissolving 26.7 grams of dicyandiamide in 395 grams of dimethyl formamide and mixing the resulting solution into 1236 grams of DER 71881 A80 epoxy resin (Dow Chemical). The following were then added to the epoxy resin mixture: 270 grams of acetone, 386 grams of ASP400 (3-5 μm aluminum silicate powder, Engelhard Corp.), 288 grams of ATH C330 (3 μm aluminum trihydrate powder, Alcoa), 42 grams of antimony trioxide, and 198 grams of Paraloid EXL2691 (core-shell particles, Rohm and Haas, 0.1 μm). Then, 1.8 grams of 2-methyl imidazole dissolved in 80 grams of acetone was added. The varnish gel time was measured to be 200 seconds at 171°C 1.5 hours after being prepared. A glass fiber mat weighing 1 gram per each 4" x 4" square (101.6 mm x 101.6 mm) was saturated with the varnish and then baked for 4 minutes at 330°F (166°C). The B-staged mat contained 87% resin and had a flow of 20.4 % when pressed for 8 minutes at 171°C and 200 psi (1379 kPa).

A copper clad laminate was made for testing by stacking 4 plies of B-staged mat 13"x13" (330 x 330 mm), placing a 1 oz/ft^2 (305 grams/m^2) copper foil on one side and a 1 mil (25 μm) thick release film on the other. The stacked layers were placed between two stainless steel caul plates and three layers of Kraft paper were placed on each side of the stack before being pressed at 300°F (149°C) for 20 minutes, and finally at 340°F (171°C) for 80 minutes, using a pressure of 250 psi (1723 kPa). The cured stack was cooled to room temperature while remaining under pressure and then cut to 12" x 12" (304 x 304 mm).

The resulting laminate was then tested using standard tests for such laminates, with the results being reported in the table below.

Example 2

The procedure of Example 1 was repeated except that the proportion of Paraloid 2691 was reduced to one-half, 10 parts per hundred of epoxy resin (phr) or 8.35 wt.% of the B-staged mat. The cured laminate was measured as before and the results are shown in the table below.

Example 3

The procedure of Example 1 and 2 was repeated except that the amount of Paraloid 2691 was cut in half again, that is to 5 pph resin or 4.18 wt % based on the B-staged mat. The properties of the cured laminate were measured and the results reported below.

Example 4 (comparative)

The experiments of the above examples were repeated except that no Paraloid 2691 was used, but instead 7.5 pph of Hycar elastomer (B.F. Goodrich) was included in the resin formulation. The finished laminate was measured as before and the results are shown below.

Example 5 (comparative)

Another laminate was prepared as in the above examples except that no Paraloid was included and no elastomer was added as in Example 4. Properties of this base laminate are reported in the table below.

Example 6

The procedure of Example 6 was repeated using 15 phr of Paraloid EXL2691 and talc (Nytal 400, 3-5 μm, R.T. Vanderbilt) was substituted for the ASP400. The laminate was tested as before, with the results shown in the table below.

Table A

	Example					
Properties	***1***	***2***	***3***	***4***	***5***	***6***
Dielectric Constant (a)	4.15	4.27	4.35	4.36	4.47	4.02
Dissipation Factor (b)	0.0208	0.0215	0.0232	0.0271	0.0227	0.0165
CTI, volts (c)	540-550	540-440	360-380	340-360	340-360	560
Solder Float @ 550 °F (288°C) (d)	58	56	40	48	29	23

Peel Strength, lbs./in (kg/mm) (e)	8 (0.143)	8.5 (0.152)	8.7 (0.156)	7.21 (0129)	9.8 (0.175)	7.6 (0.136)
Flexural Strength, psi (MPa) (f)	17125 (118)	19195 (132)	22913 (158)	21746 (150)	19915 (137)	–
Flexural Strength, psi (MPa) (g)	16855 (116)	17450 (120)	N/A	10975 (75.7)	16430 (113)	–
Tg, °C (h)	132	132	131	121	122	87
CTE below Tg, ppm/°C (I)	76.9	83.6	54	138	72.7	72.4
CTE above Tg, ppm/°C (j)	503	488	443	427	495	–
Flammability, sec (k)	0	0	0	0	0	0
Thickness, mil (mm)	75 (1.9)	75 (1.9)	70 (1.78)	–	–	53 (1.35)

(a) IPC TM 650, 1 MHz, 24 hr. 23°C, 50% relative humidity

(b) IPC TM 650, 1 MHz, 24 hr. 23°C, 50% relative humidity

(c) ASTM D 3638-85, Comparative Tracking Index

(d) time to failure, seconds

(e) IPC TM 650

(f) IPC TM 650

(g) IPC TM 650

(h) IPC TM 650 by thermomechanical analysis (Z axis) room temperature to 288°C at 10°C/min.

(i) IPC TM 650 by thermomechanical analysis (z axis) room temperature to Tg at 10°C/min.

(j) IPC TM 650 by thermomechanical analysis (Z axis) Tg to 288°C at 10°C/min.

(k) UL94, vertical

A review of the above data indicates that addition of the Paraloid core-shell particles reduces the dielectric constant and dissipation factor. Surprisingly, the Comparative Tracking Index, is substantially improved when relatively large amounts of the core-shell particles are included.

Example 8

Three formulations were prepared in which an inorganic filler was substituted for a portion of the core-shell particles. They were:

Component	T	W	TLP
DMF	100 g.	100 g.	100 g.
PM	150 g	50 g	150 g
DICY	10.9 g	10.9 g	10.9 g
2-MI	1.1 g	1.0 g	1.0 g
Paraloid EXL2691	60 g	60 g	20 g
XU71881(A8O)epoxy	500 g	500 g	500 g
Acetone	400 g	275 g	460 g
Talc (Nytal 400)	364 g	-	364 g
ATH C 330	117 g	117 g	117 g
Sb_2O_3	8.5 g	8.5 g	8.5 g
Ca silicate (Wollastocast 10734)	-	464 g	-

These formulations were used to prepare laminates as in Example 1 and tested as before, with the results shown in the following table.

Table B

Properties	Formulation T	W	TLP
CTI, volts	560	520	390
CTE, X axis	31	34	36
Y axis	53	34	36
Tg, X axis	50°C	81°C	61°C
Y axis	67°C	88°C	89°C
Solder Float @ 550°F	8 sec.	32 sec.	11 sec.
Peel Strength	6.3/6.3 lbs./in	8.2/8.1 lbs./in	6.3/6.6 lbs./in
Dielectric Constant	4.94	4.75	5.17
Dissipation Factor	0.051	0.019	0.052

From the results shown above, it may be concluded that compositions T and TLP which contain talc and no calcium silicate have undesirably low values in the solder float test. Also, reducing the amount of Paraloid (T vs. TLP) sharply reduces the CTI to an unacceptable value.

Example 9

Three similar formulations were prepared employing varying amounts of inorganic fillers, each including the polymeric filler Paraloid EXL 2691. The compositions were:

Component	A	B	TC
DMF	150 g	150 g	150 g
PM	75 g	75 g	75 g
DICY	16.4 g	16.4 g	16.4 g
2-MI	0.9 g	1.3 g	1.65 g
Paraloid EXL2691	90 g	90 g	90 g
XU71881(A8O)	750 g	750 g	750 g
Acetone	413 g	413 g	473 g
Talc (Nytal 400)	441 g	617 g	417 g
ATH C 330	176 g	-	-
Sb_2O_3	12.8 g	12.8 g	12.8 g
ASP 400	-	-	200 g

The formulations were used to prepare laminates as in Example 1 and tested as before, with the results shown in the following table.

Table C

	Formulation		
Properties	A	B	TC
CTI, volts	500	450	600
CTE,			
X axis, RT to 85°C	42.7	37.6	43.1
Y axis, RT to 85°C	40.3	33.8	26.4
Z axis, RT to 85°C	72.4	67.7	59.6
Tg, (TMA)	87°C	85°C	121°C
Solder Float @ 550°F	23 sec.	123 sec.	147 sec.
Peel Strength, TS	7.6	6.7	7.6
E 1/125	6.0	5.5	5.9
Dielectric Constant,			
Cond. A	4.02	4.04	4.08
After 3 hr. @ 105°C	3.96	4.01	4.06
Dissipation Factor,			
Cond. A	0.0165	0.0174	0.0154
After 3 hr. @ 105°C	0.0154	0.0151	0.0148

Flammability, Cond. A	0	0	0

It can be seen that composition TC has superior performance in the Comparative Tracking Index test and exhibits a good resistance in the solder float test. This composition includes talc and calcium silicate, but omits aluminum trihydrate, which is considered to be the reason for undesirably low results in the solder float test.

CLAIMS:

1. A method of reducing the dielectric constant and dissipation factor in printed circuit boards made from metal foil clad insulating substrates comprising incorporating in said insulating substrates more than zero and up to 25 wt.% of polymeric particles having an average diameter of about 0.05 to 30 μm.

2. The method of Claim 1 wherein said particles have an average diameter of about 0.05 to 5 μm.

3. The method of Claim 1 wherein said polymeric particles are core-shell particles.

4. The method of Claim 3 wherein said insulating substrates further comprise inorganic filler particles.

5. The method of Claim 3 wherein said core-shell particles comprise a core of butadiene polymer and a shell of methacrylate polymers.

6. The method of Claim 5 wherein about 3 to 20 wt.% of said particles are added to epoxy resin and cured to form said insulating substrate.

7. The method of Claim 6 wherein said epoxy resin containing said particles is applied to glass fiber reinforcing material, cured, and used in manufacture of said printed circuit boards.

8. A method of increasing the Comparative Tracking Index of insulating substrates used in printed circuit boards comprising incorporating in said insulating substrates more than zero and up to 25 wt.% of polymeric particles having an average diameter of about 0.05 to 30 μm.

9. The method of Claim 8 wherein said particles have an average diameter of about 0.05 to 5 μm.

10. The method of Claim 8 wherein said polymeric particles are core-shell particles.

11. The method of Claim 10 wherein said core-shell particles comprise a core of butadiene polymer and a shell of methacrylate polymer.

12. A laminate for use in printed circuit boards comprising an insulating substrate comprising an inner glass fiber reinforced epoxy resin containing more than zero and up to 25 wt.% of polymeric particles having an average diameter of about 0.05 to 30 μm and covered with layers of glass fiber reinforced epoxy resin.

13. laminate of Claim 12 wherein said particles have an average diameter of about 0.05 to 5 μm.

14. A laminate of Claim 12 wherein said insulating substrate further comprises inorganic filler particles.

15. A laminate of Claim 14 wherein said inorganic filler particles are talc and aluminum silicate.

16. A laminate of Claim 12 wherein said polymeric particles are core-shell particles.

17. A laminate of Claim 16 wherein said core-shell particles comprise a core of butadiene polymer and a shell of methacrylate polymer.

18. A laminate of Claim 12 wherein said insulating substrate comprises a cured glass-reinforced epoxy resin.

19. A laminate of Claim 18 wherein said particles comprise about 3 to 20 wt.% of said substrate.

20. A laminate of Claim 12 wherein said inner glass fiber reinforced epoxy resin is a woven glass fiber epoxy resin and said covering glass fiber reinforced epoxy resin is a non-woven glass fiber epoxy resins.

21. A laminate of Claim 12 wherein said inner glass fiber reinforced epoxy resin is a non-woven glass fiber reinforced epoxy resin and said covering glass fiber reinforced epoxy resin is a woven glass fiber reinforced epoxy resin.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/16400

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H05K1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 8832 Derwent Publications Ltd., London, GB; AN 88-224301 XP002022154 & JP,A,63 159 441 (SUMITOMO BAKELITE KK) , 2 July 1988 see abstract	1,2
A		6,7,12, 13,18

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
7 January 1997	23.01.97

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 8831 Derwent Publications Ltd., London, GB; AN 88-217586 XP002022155 & JP,A,63 154 748 (SUMITOMO BAKELITE KK) see abstract	1,2
A		6,7,12, 13,18
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X	PATENT ABSTRACTS OF JAPAN vol. 15, no. 130 (E-1051), 29 March 1991 & JP,A,03 014282 (MITSUBISHI ELECTRIC CORP), 22 January 1991, see abstract	1,2
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A		6,7,12, 18
X	DATABASE WPI Week 9330 Derwent Publications Ltd., London, GB; AN 93-239607 XP002022158 & JP,A,05 162 240 (MATSUSHITA ELECTRIC WORKS) , 29 June 1993 see abstract	1
A		6,7,12, 18

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/16400

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	POLYMER, vol. 34, no. 7, March 1993, pages 1695-1701, XP000609999 B.J. CARDWELL ET AL.: "Rate and temperature effects on the fracture toughness of a rubber-modified epoxy" cited in the application see page 1695	1-3,5
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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